

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Calcium Silicate Product and Method of Preparing Same

We, JOHNS-MANVILLE CORPORATION, a corporation organized under the laws of the State of New York, United States of America, of 22 East 40th Street, City of New York, County of New York and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to improved hydrated calcium silicate products and their preparation. More particularly, the invention is concerned with an improved method of buffering the basic characteristics of hydrated calcium silicates and products thereof.

Particulate hydrated calcium silicates have for some time been proposed for use as fillers, pigments, extenders, etc., for paint, paper, rubber plastic, and the like products and in some applications such silicates have been found effective to varying degrees. However, many calcium silicate compositions now available typically exhibit one or more properties such, for example, as relatively high solubilities, high alkalinity or basic pH, among others, which render them unsatisfactory and/or impractical, in many applications or products wherein a substantially completely insoluble or "inert" and/or approximately neutral or even acid filler or pigment possessing other properties not unlike those of the highly absorptive calcium silicates could effectively and economically fulfill many filler, pigment or extender requirements in the paint, paper, rubber, plastic and allied industries.

The invention relates to a method and to the particulate hydrated calcium silicate product produced thereby characterized in that stable, hydrothermally formed, high temper-

ature phase hydrated calcium silicates are hydrothermally reacted with aluminum sulfate at a temperature of at least 350°F., preferably between 450°F. to 550°F. in an amount equivalent to and for a period sufficient to effect reaction with at least 5%, preferably 7-1/2% to 60%, by weight of the total CaO component of the hydrated calcium silicates, the hydrated calcium silicates being selected from the group consisting of xonotlite and a synthetic hydrated calcium silicate having the composition $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 1-2 \cdot 5\text{H}_2\text{O}$, and mixtures thereof; the product produced thereby exhibits an "alum demand" no greater than 4 milliliters of an aqueous solution of 0.0216 grams of aluminum sulfate per milliliter to achieve a pH of about 5.

Fig. 1 of the accompanying drawings illustrates the relative effectiveness of the treatment of this invention and the pH characteristics of the products of said treatment in comparison with those of procedures not within the scope of this invention;

Fig. 2 illustrates the unreceptiveness of low temperature phase hydrated calcium silicate products such as calcium silicate hydrate I to all types of treatment including the novel method of this invention;

Fig. 3 compares the relative effectiveness of the method of this invention as applied to various high temperature phase hydrated calcium silicate compositions; and

Fig. 4 illustrates the long term alum stability of products treated in accordance with this invention.

Typical hydrated calcium silicate products when subjected to an aqueous acid medium in the performance of a process or in the preparation of a product, for example a paper-making furnish wherein alum (aluminum sulfate) is often added to maintain the pH of the furnish within the approximate range of

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4—6, react with the acidic component(s) of said medium with a resultant overall increase in pH. Thus, whenever essential, or even desirable to maintain or restore the low pH condition of the medium, an additional amount of the acidic or acid producing component must be added to restore or maintain the pH at the desired or original level. Such a practice is often costly and therefore prohibitive in many manufacturing procedures or products.

This invention provides new hydrated calcium silicates exhibiting relatively low pH characteristics, among other advantageous properties, which are peculiarly adaptable for use as fillers, pigments, extenders, in products or processes involving or necessitating relatively low or acid pH mediums. This novel silicate products of this invention are produced by hydrothermally reacting stable, high temperature phase hydrated calcium silicate compounds with aluminum sulfate at temperatures of at least 350°F. and preferably within the range of 450° to 550°F. A temperature of about 450°F. is most preferred for reasons of efficiency and economy. Further, the treatment or reaction should comprise sufficient aluminum sulfate and be permitted to proceed to a point wherein at least 5% by weight of the calcium oxide component of the particular silicate has reacted with aluminum sulfate, it being understood that the theoretical stoichiometric proportions of aluminum sulfate and calcium oxide comprise 1 mol of aluminum sulfate per 3 mols of calcium oxide. The degree to which it is desirable or appropriate to extend the aluminum sulfate treatment beyond the foregoing stated 5% minimum, however, depends upon the requirements desired to the ultimate product.

As stated hereinbefore the high temperature aluminum sulfate treatment of this invention is only effective when applied to high temperature phase hydrated calcium silicate compounds, viz., hydrothermal reaction products of an aqueous suspension of lime and a reactive siliceous material, such as diatomaceous earth, quartz, etc., at temperatures of at least 350°F. and preferably approximately 450°F. Exemplary of suitable high temperature phase calcium silicate compounds are the calcium silicate xonotlite ($5\text{CaO} \cdot 5\text{SiO}_2 \cdot \text{H}_2\text{O}$) and a very low solubility calcium silicate compound having the formula $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 1\text{--}2 \cdot 5\text{H}_2\text{O}$ and a distinguishing X-ray diffraction pattern having very strong lines $d=3.12\text{\AA}$ and $d=4.12\text{\AA}$ and a medium line at $d=8.34\text{\AA}$. The foregoing high temperature phase compounds may be prepared by the hydrothermal reaction of lime and a source of reactive silica in the respective mol ratios of 1 mol of CaO per mol of SiO_4 and 0.5—0.7 mols of CaO per mol of SiO_4 in aqueous suspension at temperatures of at least 350°F., pre-

ferably 450°F., for periods typically of about 2 hours. By varying the mol ratios of the reactive lime and siliceous components calcium silicate products comprising mixtures of the various stable, high temperature phase hydrated calcium silicates may be produced and such mixtures are likewise applicable in the practice of this invention.

The extent to which the foregoing aluminum sulfate treatment of the hydrated calcium silicate may be effected depends, naturally, upon the relative proportions or mol ratios of aluminum sulfate added to the calcium silicate compound and as such can range from uneconomical stoichiometric proportions, i.e., substantially complete or total reaction or consumption of all the available calcium oxide component of the calcium silicate consisting of 1 mol of $\text{Al}_2(\text{SO}_4)_3$, per 3 mols of CaO, down through any proportions or percentages thereof to the lowest effective limit of at least 5% of the calcium oxide content of the particular calcium silicate compound. Suitable aluminum sulfate treated calcium silicate products for many applications comprise those resulting from a treatment with sufficient aluminum sulfate to react with approximately 7-1/2% of the available calcium oxide of the particular silicate (i.e., about 0.025 mols $\text{Al}_2(\text{SO}_4)_3$ per mol of CaO).

The effectiveness of the foregoing aluminum sulfate treatments as well as that of previous methods, i.e., the extent or degree to which said treatments reduce or suppress the basic pH characteristics of the treated calcium silicate product, may be measured by the amount of aluminum sulfate required either to reduce a slurry or a given amount of an aluminum sulfate treated calcium silicate to a predetermined pH, or to maintain a predetermined maximum pH for a slurry or aqueous medium following the addition thereto of an aluminum sulfate treated calcium silicate. The effectiveness or extent which the treatment reduces or suppresses the basic pH characteristics of the treated calcium silicate and appropriate means for measuring the same are referred to hereinafter as the "alum demand" of the aluminum sulfate treated or buffered calcium silicate. The specific test utilized in determining the "alum demand" of the treated calcium silicates in the following examples and throughout the specification, unless indicated otherwise, comprises adding to a 1/2 gram sample of the particular aluminum sulfate treated calcium silicate slurried in 400 milliliters of water, 1 milliliter increments of aluminum sulfate solution containing 0.0216 grams of hydrated aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) per milliliter and determining the pH after stirring for 5 minutes. The "alum demand" is expressed as the milliliters of aluminum sulfate solution which must be added to reduce the pH of the slurry to 5.0.

The aluminum sulfate treatment of stable, high temperature phase hydrothermally prepared hydrated calcium silicate compounds may be effected in substantially any convenient or appropriate manner it being essential only that the high temperature phase hydrated calcium silicate and aluminum sulfate are hydrothermally reacted, preferably in aqueous medium, at temperatures of at least 350°F. and preferably 450 to 550°F. Moreover, the aluminum sulfate treatment may be practically and economically carried out in the same reactor vessel or chamber utilized to synthesize the high temperature calcium silicate simply by adding an aqueous solution of aluminum sulfate directly to said reactor upon substantial completion of the hydrothermal formation of the hydrated calcium silicate product and maintenance of the synthesizing temperatures. Such a procedure, addition of the aluminum sulfate directly to the hot reactor vessel contents, provides a substantial savings over subsequent heating of all components to a suitable reaction temperature.

The aluminum sulfate reagent suitable for carrying the invention into effect may comprise ordinary "paper-maker's alum" or any of the commercial grades of aluminum sulfate available on the market.

The mechanism of this invention being somewhat problematical, the following theoretical explanation is given for purposes of illustration rather than limitation. However, extensive observations indicate that the treatment of stable, high temperature phase hydrated calcium silicates with aluminum sulfate at the specified necessary temperatures results in a reaction product(s) of the aluminum sulfate and calcium silicate forming a protective coating on or modification of the surfaces of the hydrated calcium silicate particles providing the same with effective resistance from further acid attack.

The following examples illustrate the present invention including several variations in the practice of the same.

EXAMPLE I

Eighty-five pounds of diatomaceous earth suspended in 60 gallons of water was charged to a reactor, steam pre-heated to a temperature of 450°F. and drained of condensate. Upon return of the reactor temperature to 450°F., 100 pounds of hydrated lime in 60 gallons of water (giving a calculated CaO/SiO₂ mol ratio of approximately 1.0) was added thereto and the temperature again raised to 450°F. and maintained there for about 1-1/2 hours. Finally, 18-1/2 pounds of paper-maker's alum in 40 gallons of water (0.024 mols of hydrated aluminum sulfate per mol of CaO) was added to the reactor and maintained therein for approximately 1/2 hour for a total reaction time of 2 hours at a temperature of 450°F. The product was then drained into a holding tank and filtered over a rotary vacuum filter, oven dried and pulverized.

EXAMPLE II

An aluminum sulfate treated xonotlite calcium silicate was prepared by maintaining an aqueous suspension of 1800 gallons of diatomaceous earth slurry comprising 0.63 pounds of diatomite per gallon and about 680 gallons of lime slurry comprising 1.46 pounds of CaO per gallon in a reaction vessel for 1-1/2 hours at a temperature of about 460°F. The relative proportions of lime and siliceous components thereof were calculated to give a CaO/SiO₂ mol ratio of 1.0. Upon completion of the reaction comprising 1-1/2 hours at temperatures of about 460°F., an aqueous solution of aluminum sulfate comprising 2.0 pounds per gallon was added to the reaction vessel until the aluminum sulfate content thereof reached 2.4 pounds per pound of CaO component of the calcium silicate (about 0.20 mols of hydrated aluminum sulfate per mol of CaO) and the combined reaction mixture was maintained at a temperature of approximately 460°F. for an additional period of about 30 minutes. The contents of the reactor were then filtered, dried and ground.

EXAMPLE III

A suitable high pressure reactor vessel was first pre-heated with steam to a temperature of approximately 450°F. and upon draining of the condensate was charged with 85 pounds of diatomaceous earth suspended in 60 gallons of water and the temperature was brought back to 450°F. One hundred pounds of hydrated lime, also suspended in 60 gallons of water, was then charged to the reactor and the temperature again raised to 450°F. and held there for a 2 hour reaction period. The relative proportion of lime and siliceous material was calculated to give a CaO/SiO₂ mol ratio of 1.0. Upon completion of the reaction period the reaction product was drained into a holding tank and the total solids in the reactor slurry were determined by evaporating a known volume of the slurry to dryness to calculate the hydrated calcium silicate content thereof for subsequent treatment. Sufficient aluminum sulfate to react with about 15% of the CaO content of the calcium silicate (0.237 pounds of hydrated aluminum sulfate per pound of hydrated calcium silicate) was dissolved in about 20 gallons of water and added to the aqueous suspension of hydrated calcium silicate in the holding tank with continuous stirring and the contents thereof maintained at a temperature of about 160°F. for 1 hour. This addition of aluminum sulfate treating agent caused the slurry to thicken considerably and it was necessary to add additional water, about half the initial slurry volume, to keep the slurry

in workable condition. The treated product was filtered over a rotary vacuum filter, dried at 240°F. in an oven and ground.

The "alum demand" of the products of Examples I and II, comprising a 7-1/2% and a 60% aluminum sulfate treated xonotite in accordance with this invention, Example III, comprising a 7-1/2% conventionally treated xonotite, and an untreated xonotite as a standard were determined in accordance with the foregoing stated procedure, i.e., titrating 1 milliliter increments of aluminum sulfate solution containing 0.0216 grams of hydrated aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) per milliliter against a 1/2 gram sample of each of the specified aluminum sulfate treated calcium silicate products and the untreated xonotite slurried in 400 milliliters of water and determining the pH after stirring for 5 minutes. The results of the foregoing test were plotted on a graph for comparison of the "alum demand" of the untreated calcium silicate xonotite and those treated, according to prior practices. These results comprise the graph of Fig. 1. The "alum demand" is expressed as the milliliters of aluminum sulfate solution which must be added to reduce the pH of the slurry to 5.0.

EXAMPLE IV
 Three identical samples of a low temperature phase hydrated calcium silicate compound identified in the art as the phase calcium silicate hydrate I (Taylor, *Journal of the Chemical Society, (United States of America)*, 163, 1953) were prepared by reacting hydrated lime and a siliceous material in a mol ratio of 0.6 CaO to 1 SiO₂ at a temperature of 350—360°F. for a period of about 2 hours. Sample 1 was retained untreated as a standard. The second sample was treated with sufficient aluminum sulfate to react with 7-1/2% of the lime content thereof at ambient temperatures. The third sample was retained in the reactor and treated with sufficient aluminum sulfate to react with 7-1/2% of the lime content thereof at temperatures in the vicinity of 350—360°F. The "alum demand" of each sample, determined exactly in accordance with the foregoing procedure, was plotted for comparison and comprises the graph of Fig. 2 of the drawing. This experiment accordingly demonstrates that only the high temperature (above 370°F., preferably approximately 450°F.) phase calcium silicates can be made resistant to acidic conditions by treatment with aluminum sulfate.

EXAMPLE V
 A series of hydrothermal synthesis of high temperature phase hydrated calcium silicate products comprising reacting lime and siliceous reactants in CaO/SiO₂ mol ratios varying progressively from 0.5 to 1.0 CaO to

1 SiO₂ at temperatures of about 450°F. for a period of about 1-1/2 hours was effected. Each of the resulting hydrated calcium silicate products thereof, comprising either xonotite, the low solubility calcium silicate having the formula $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 1-2 \cdot 5\text{H}_2\text{O}$ referred to hereinbefore or mixtures of the said compounds, were treated by adding sufficient aqueous aluminum sulfate to the reactor vessels to react with 7-1/2 of the calcium oxide content of the specific compound and continuing the reactions for periods of about 1/2 hour and at temperatures of approximately 450°F. The decreasing CaO/SiO₂ mol ratios of the hydrated calcium silicate resulted in only a very slight increase in "alum demand". The "alum demand" of each of these products, determined in accordance with the foregoing test, is plotted in the graph of Fig. 3.

EXAMPLE VI

Six identical samples of the high temperature phase calcium silicate xonotite were prepared in accordance with the hydrothermal procedure and aluminum sulfate treatment of Example II. The respective xonotite samples were treated with aluminum sulfate to varying degrees by maintaining each in an aqueous medium for a period of about 1/2 hour at a temperature of approximately 450°F. with sufficient aluminum sulfate reagent to react with 7-1/2%, 30%, 40%, 50%, 60% and 90% of their CaO content. The long term "alum demands" for each of thus prepared aluminum sulfate treated calcium silicate samples was determined for comparison and evaluation by slurring 0.50 grams of each of said samples in 400 milliliters of water, adding aluminum sulfate to each slurred sample in amount equivalent to 0.086 pounds per pound of calcium silicate and measuring and recording the pH of each slurry sample as a function of time. The results of these tests, shown in Fig. 4, illustrate the lasting low pH properties imparted by the 60% treatment. Because of the large differences in the stability of these samples the time is plotted on a logarithmic scale.

EXAMPLE VII

A low solubility high temperature phase hydrated calcium silicate having the formula $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 1-2 \cdot 5\text{H}_2\text{O}$ was treated with 21.8 pounds of paper-maker's alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) per 100 pounds of the lime component in a hydrothermal reaction vessel for a period of 30 minutes at a temperature of about 450°F. This is sufficient aluminum sulfate to react with approximately 7-1/2% of the CaO content of the calcium silicate. A comparison of the filtration rate of the foregoing alum treated hydrated calcium silicate was made with an identical untreated low solubility high temperature phase

hydrated calcium silicate compound. Under identical conditions the filtration rate of the aluminum sulfate treated product was 17.4 pounds per hour per square foot whereas the untreated product gave a filtration rate of 7.95 pounds per hour per square foot.

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EXAMPLE VIII

Several 5 gallon pressure reactors were each charged with 438 grams of diatomaceous earth, 151 grams of hydrated lime and 3-1/2 gallons of water to provide a CaO/SiO₂ mol ratio of 1.0, and upon completion of each 90 minute reaction period at 450°F. producing the stable high temperature phase hydrated calcium silicate xonotlite, aluminum sulfate was added to each reactor in 1/2 gallon of water and after an additional 1/2 hour reaction at 450°F. the product was drained from each reactor, filtered, dried and ground. For purposes of illustration the aluminum sulfate treatments were carried out at theoretical levels of 3, 6 and 30% of the amount of aluminum sulfate required to react with the CaO content of the calcium silicate (a 100% aluminum sulfate treatment requiring 1 mol of aluminum sulfate per 3 mols of calcium oxide of the calcium silicate product). When 6% or greater aluminum sulfate was used, the final "alum demand" of the product was found to be

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less than 0.14 pounds aluminum sulfate per pound of calcium silicate, at the 3% level of treatment the "alum demand" was considerably higher.

WHAT WE CLAIM IS:—

1. A method of preparing a particulate hydrated calcium silicate product characterized in that stable, hydrothermally formed, high temperature phase hydrated calcium silicates as hereinbefore defined are hydrothermally reacted with aluminum sulfate at a temperature of at least 350°F., preferably between 450°F. to 550°F. in an amount equivalent to and for a period sufficient to effect reaction with at least 5%, preferably 7-1/2% to 60%, by weight of the total CaO component of the hydrated calcium silicates. 40

2. A method as recited in claim 1, characterized in that the hydrated calcium silicates are xonotlite or synthetic hydrated calcium silicate having the composition 2CaO . 3SiO₂ . 1—2 . 5H₂O or mixtures thereof. 45

3. A particulate hydrated calcium silicate produced by the method recited in any of claims 1 and 2. 50

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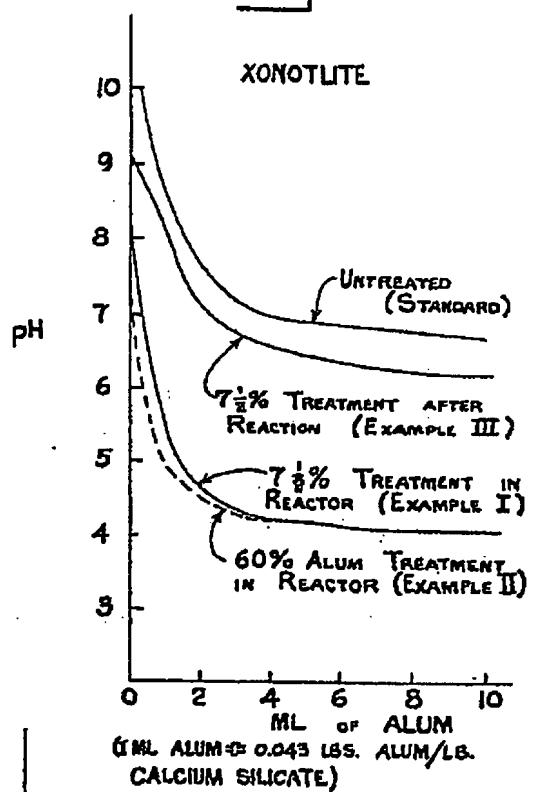
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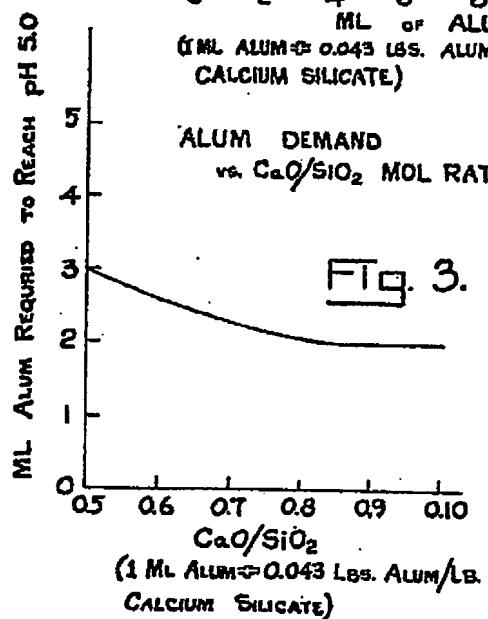
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Fig. 1.



ALUM DEMAND
vs. CaO/SiO_2 MOL RATIO



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 SHEETS 1 & 2

FIG. 2.

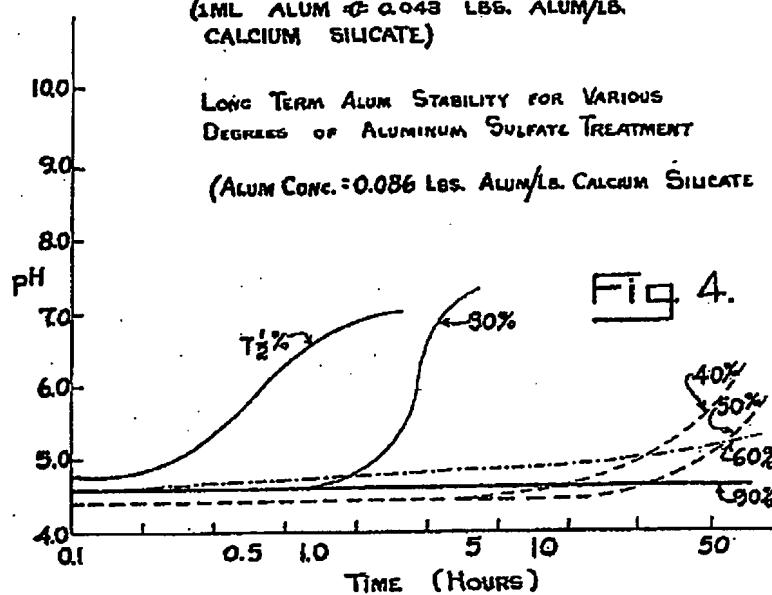
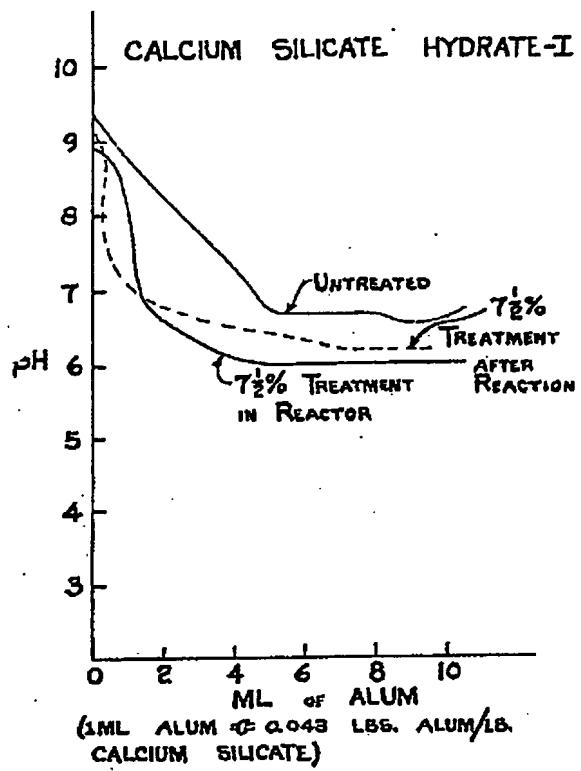


FIG. 4.

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FIG. 1.

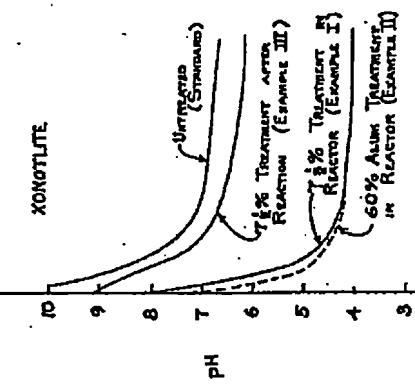


FIG. 3.

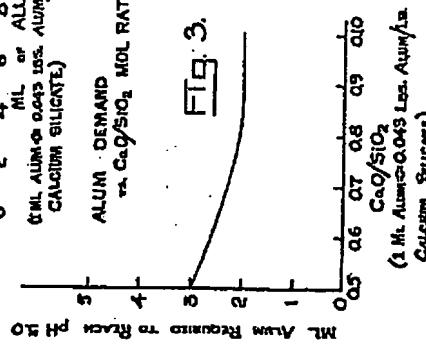
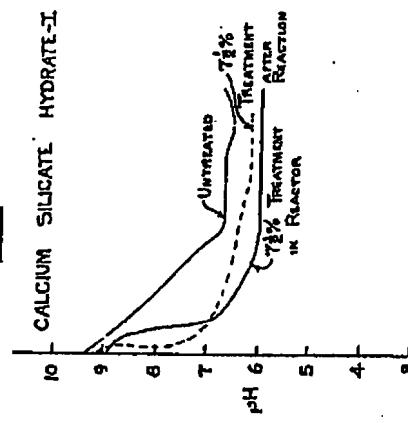


FIG. 2.



Long Term Alum Stability for Various
Doses of Aluminum Sulfate Treatment
(Alum Concentration 10.086 lbs. Alum/lb. Calcium Silicate)

FIG. 4.

